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(54) Title: HIGH MELT STRENGTH POLYPROPYLENE, CONTINUOUS PROCESS FOR THE PRODUCTION THEREOF, AND MOLDED ARTICLE			
(57) Abstract <p>A high melt strength polypropylene of wide or bimodal molecular weight distribution is described, which imparts to the product rheological characteristics such as it can be formed in machines normally used for resins such as polystyrene. Molded articles produced from the inventive polypropylene are also described. Also described is a continuous process for producing the high melt strength polypropylene which is obtained in the presence of a Ziegler-Natta type catalyst system, using at least two polymerization vessels connected in series, the control of the molecular weight being effected by the addition of discrete amounts of a molecular weight regulator, such as hydrogen, to at least one of the various polymerization vessels, so as to obtain in the first polymerization vessel a portion of higher molecular weight and in the following polymerization vessels, polymer portions of lower molecular weight, whereby the total polymer shows a wide or bimodal molecular weight distribution, which impart to the product interesting rheological properties.</p>			

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Specification of the Patent of Invention "HIGH MELT STRENGTH POLYPROPYLENE, CONTINUOUS PROCESS FOR THE PRODUCTION THEREOF, AND MOLDED ARTICLE"

5 FIELD OF THE INVENTION

This invention relates to a high melt strength polypropylene with a molecular weight distribution—which-leads-to-rheological characteristics that renders it especially suited for thermoforming, sheet forming and blow molding. More specifically, the present invention relates to a polypropylene with characteristics derived from its high melt strength which 10 enables the production, by molding it pure or compounded with mineral fillers, of molded articles with excellent appearance, while of inferior cost as compared to those presently molded from polystyrene.

The present invention also relates to a continuous process for producing the inventive high melt strength polypropylene. More specifically, the present invention relates to a 15 continuous propylene polymerization process in the presence of a Ziegler-Natta catalytic system, the process making use of at least two polymerization vessels connected in series, while discrete amounts of a molecular weight regulator such as hydrogen are added to at least one of the polymerization vessels to produce high melt strength polypropylene.

20 BACKGROUND OF THE INVENTION

Although polypropylene is a widespread, cheap and well-known plastic material, its high crystallinity requires special machinery for its processing, such as accurate and expensive to produce a polypropylene which could be processed in machinery not provided for with stringent, accurate temperature controls. A high melt strength polypropylene would 25 correspond to such requirements. Several documents of the technical and patent literature report the search for such a high melt strength polypropylene.

European Patent EP 98968 describes a polypropylene obtained by polymerizing propylene or propylene and ethylene, in several steps or stages in the presence of a catalyst which comprises a titanium trichloride composition, an aluminum compound and a molecular 30 weight regulator, characterized in that the ultimate or total polymer which comprises a higher molecular weight polymer and a lower molecular weight fraction has a melt index (MI) of from 0.03 to 2.0 g/10 min; while between this melt index and the HMI (determined at 10.8 kg/10 min, 230 °C) obtained under a load 5 times higher than that used for the MI, there is the

relationship:

$$\log \text{HMI} > 0.922 \log \text{MI} + 1.44.$$

5 Considering the intrinsic viscosity (as measured in tetralin at 135 °C) of the higher molecular weight portion is n_H and that of the lower molecular weight portion is n_L , then these two viscosities should satisfy the following equation

$$3.0 < n_H - n_L < 6.5$$

10

wherein the total polymer comprises 35 to 65% by weight of a polymer portion corresponding to the higher molecular weight portion and 65 to 35% by weight of a polymer portion which corresponds to the lower molecular weight portion. Propylene is adequately copolymerized with ethylene in at least one of the multiple stages and ethylene content in the total polymer is adequately of from 1 to 15% by weight.

15

Example 1 of European EP 96968 describes a batch polymerization process in two stages, wherein the concentration of gas phase hydrogen is of 5.5% in the first stage. When the amount of polymerized propylene reaches 3 kg, polymerization is stopped and the polymer is submitted to analysis; then, polymerization is reassumed (2nd stage) at the same propylene pressure (10 kg/cm²) of the first stage while keeping the concentration of gas phase hydrogen at 0.2%.

20

When additional 3 kg of polymer are produced, slurry polymerization is stopped again in order to ascertain properties such as yield and intrinsic viscosity. It is alleged that this procedure leads to a product with excellent thermoforming properties. Other Examples of the 25 patent are described in which ethylene incorporated in a third polymerization stage, always in batch mode.

30

European Patent EP 98077 claims a polypropylene obtained by submitting propene to a multiple stage polymerization in the presence of a catalyst prepared through the reaction of an organoaluminum compound (I) or a reaction product (VI) of an organoaluminum compound (I) with an electron donor (A) with TiCl₄ reacting the solid resulting product (II) with an electron donor (A) and an electron acceptor (B); and combining the solid resulting product (III) with an organoaluminum (IV) and an ester of an aromatic carboxylic acid (V), the molar ratio of compound (IV) to the solid product (III), Al/Ti; being in the range of 0.1 to 100/1.

Compound (IV) has the general formula $Al R_a R'_n X_{3-(n-m)}$ and the molar ratio (V:III) of the aromatic carboxylic acid ester to the solid product (III) is in the range of 0.1 to 10.0. In this polymerization, the amount of propylene polymerized at the first stage is adjusted so as to constitute 35 to 65% by weight based on the total amount polymerized and, in the second stage et seq., it is controlled so as to constitute 65 to 35% by weight based on the total product. The intrinsic viscosity values of the respective polymer portions are also adjusted in order to satisfy the equation

$$3.0 < n_H - n_L < 6.5 \quad (1)$$

10

wherein n_H is the intrinsic viscosity of the higher molecular weight portion and n_L is the intrinsic viscosity of the lower molecular weight portion, the portions being those formed in the first stage and those formed in the second and subsequent stages.

15 In the preferred embodiment of EP 98077, the amount of polymer portion from the first stage (A) is nearly equal to that from the second stage (B) and concretely the amounts are both in the range of 35 to 65% by weight based on the total weight of (A) and (B), preferably 40 to 60% by weight. If the ratio of the amounts of (A) and (B) exceeds the above-mentioned range, the resulting polypropylene does not present sufficient melt flow properties, the kneading effectiveness at the time of granulation is insufficient and it is not only difficult to 20 obtain a homogeneous molded product, but also the extent of improvement in the melt viscoelasticity is small. Further, the difference between the molecular weights of the two portions should be within a range of definite values as described above in equation (1), this polymerization condition being therefore fulfilled by adjusting the concentration of gas phase hydrogen. The process disclosed in EP 98077 involves batch polymerization in bench scale.

25 In US patent 4,760,113 a continuous process for producing a high melt viscoelastic ethylene-propylene copolymer which produces a block ethylene-propylene copolymer having superior physical properties suitable for sheet molding and blow molding and capable of producing large-size molded articles is provided. The process comprises feeding ethylene and propylene in a weight proportion of 0.5% of ethylene based on the total of propylene and ethylene, into three or more polymerization vessels connected in series, to carry out continuous 30 polymerization step (1) and successively feeding ethylene and propylene in a weight proportion of 10-100% of ethylene based on the total of ethylene and propylene into one or more polymerization vessels, to carry out continuous polymerization process (ii); (b) feeding the

total quantity of the catalyst only to the first polymerization vessel; (c) feeding the total quantity of hydrogen substantially only to the first polymerization vessel; and (d) assuring that the quantity of polymer obtained in step (i) is 60-95 weight % based on the total polymerization quantity.

5 The catalyst of US 4,760,113 comprises an organoaluminum compound (B) to be combined with a titanium containing solid component (A) constituting a Ziegler-Natta type catalyst, the compound being expressed by the formula $Al\ R_m\ X_{3-m}$, polymerization being carried out in the presence of an inert solvent or liquid propylene and a glycol ether (C) which is continuously added to the polymerization reaction slurry after completion of step (i), so as to
10 give a ratio (mol/atom) of (C) to Ti in (A) of 0.01 to 1.0 in order to carry out said continuous polymerization step (ii). In the polymerization step (ii), since the ethylene concentration in the fed monomers is much different from that in step (i), the withdrawn slurry from the polymerization step (i) is received into a pressure drop vessel and subjected to degassing (removal of dissolved propylene, ethylene and hydrogen), followed by feeding the resulting
15 slurry to the polymerization vessel of the polymerization step (ii). The addition of Glycol ether (C) effected for reducing the activity of the catalyst to a considerable extent, and thereby homogenize the polymers formed in the second step. It is alleged that the product shows excellent results regarding quality and processing effectiveness of molded products.

Japanese Patent application JP 87/124108 discloses a viscoelastic polypropylene of
20 broad molecular weight distribution prepared by a slurry or mass continuous polymerization process in the presence of a Ziegler-Natta type catalyst and three polymerization vessels, the catalysts, reaction products and hydrogen in the first polymerization vessel being continuously and sequentially transferred to the second and third polymerization vessels.

Propylene pressure is increased from the first to the second polymerization vessel and from this
25 latter to the third polymerization vessel, whereby widening the molecular weight distribution. The catalyst comprises an electron donor which is diisoamyl ether.

Japanese Patent Application JP 87/195007 discloses a polymerization process analogous to that of JP 87/124108 with the exception that it
30 employs an aromatic ester such as methyl p-toluate to prepare the catalyst, thus improving the mechanical strength of the molded product, as expressed by the Young modulus which is higher for the aromatic ester modified product.

Thus, upon studying the technical literature, it is clear that the various processes and catalysts employed in the production of high melt strength polypropylene homo- or copolymers

present various drawbacks, either due to the industrial implementation of such processes, for example when they are carried out batchwise, as is the case for EP 96968 and EP 98077, or either due to the catalyst complexities or still, due to the inherent difficulties of a continuous copolymerization process using pressure drop vessels and an additive to reduce the catalyst 5 activity as in US 4760113. Moreover, in order to obtain better properties of the end product, it is advisable to have a weight proportion of at least 35%, and even 40 to 50%, of the higher molecular weight product in the total polymer. Thus, a process is needed for the homo or copolymerization of propylene in the presence of a Ziegler-Natta type catalyst which would produce a high melt strength polypropylene of improved processing behavior, such process 10 being provided for by the present invention.

Therefore, an objective of the present invention is a polypropylene of high melt strength, with rheological properties such that it is especially suitable for several forming techniques, being even a substitute for polystyrene in several applications.

Another objective is a high melt strength polypropylene, suitable for producing molded articles of excellent shape and appearance which can be transformed in machinery normally used for processing more rigid resins, of less stringent temperature requirements. 15

Another objective of the present invention is a continuous process for preparing polypropylene and optionally its copolymers having wide or bimodal molecular weight distribution, wherein the molecular weight is controlled so as to obtain polymer portions of 20 different molecular weights, wherein the ratio of the molecular weights of the portions produced in the first and in the further reactors lead to a high melt strength polypropylene.

Another objective is still to improve the thermal and mechanical properties of polypropylene molded articles by incorporating mineral fillers such as talc and calcium carbonate thereto. 25

SUMMARY OF THE INVENTION

This invention refers to a polypropylene of wide or bimodal molecular weight distribution which confers excellent thermoforming characteristics to the polymer product, whereby it is uniformly distributed in the final molded article which results in excellent shape 30 and appearance.

The inventive propylene is still distinguished by the fact that its rheology makes it possible the processing thereof in more simple machinery with less accurate temperature control means than those normally used for molding polypropylene.

The polypropylene of the invention is suitable for the production of post-processed sheets and for blow molding and is prepared in the presence of a Ziegler-Natta catalyst system and a molecular weight modifier, the total polymer comprising a portion of higher molecular weight and a portion of lower molecular weight and presenting a melt index M.I. < 3,0 g/10 min as measured at 230 °C/2.16 kg, the higher molecular weight fraction having M.I. < 1.0 g/10 min as measured at 190 °C/10 kg, the portion of higher molecular weight comprising from 10 to 35 wt% of the total polymer and the portion of lower molecular weight comprising from 65 to 90 wt% of the total polymer.

The present invention also provides for a continuous process for preparing propylene homopolymers, using at least two polymerization vessels connected in series, in the presence of a Ziegler-Natta catalyst system while adding discrete molar amounts of a molecular weight modifier to at least one of the various polymerization vessels so as to produce a polymer portion of higher molecular weight and a polymer portion of lower molecular weight, the polymer product so obtained having high melt strength, which allows its processing in machinery normally used only for more rigid and tougher resins.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematic flow sheet of an embodiment of the present invention showing five polymerization vessels connected in series and a container for the addition of catalyst and diluent suitable for slurry polymerization. Each of the illustrated polymerization vessels comprises the addition of propylene while in the last three polymerization vessels the addition of ethylene as a comonomer is optionally contemplated.

FIGURE 2 is a plot of viscosity vs shear rate for a commercial polypropylene of Melt Flow Index 2.2 and the polypropylenes of Examples 1 and 2 of the invention, measured at 230 °C.

FIGURE 3 shows the molecular weight distribution for the polypropylene according to Example 1 as measured by Gel Permeation Chromatography (G.P.C.). The two peaks of the correlation curve, respectively near 500,000 and 1,000,000, clearly demonstrate the fact that the product being bimodal. For the sake of illustration, FIGURE 4 shows the molecular weight distribution for a commercial polypropylene, this curve not showing any multiple peaks.

FIGURES 5, 6, 7, 8 and 9 are illustrative of dynamic viscoelastic tests on the inventive polypropylenes as compared to commercial counterparts. Data were collected with the aid of a mechanical spectrophotometer made by Rheometrics, model RMS 800, the test temperature

being kept always at 180°C. These Figures show the dependence of three viscoelastic variables, the Storage Modulus G', the Loss Modulus G" and the complex viscosity n^* on the shear rate as measured by means of an oscillatory effort made on the sample.

FIGURE 5 illustrates a comparison between the viscoelastic data for two commercial 5 polypropylenes, one of them indicated as Commercial PP 1 having Melt Flow Index (M.F.I.) around 1.6 while the other one indicated as Commercial PP 2 has M.F.I. around 2.2, both Indices being determined at 230°C and 2.16 kg. Corresponding curves for the features of both samples show the same general shape, with one curve slightly displaced as to the other one. This behavior indicates similar processability for both polypropylenes, their thermoforming 10 properties being inferior to the products of the invention.

FIGURE 6 compares the viscoelastic behavior of samples produced according 15 the Example 1 of the invention and Commercial PP 2. In this case correlation curves for the viscoelastic properties for the samples of the various polypropylenes show a significantly different behavior. Thus, while the Loss Modulus G" and the complex viscosity n^* for Example 1 of the invention are higher at lower frequencies, this behavior is changed at high frequencies. As regards the Storage Modulus G', for Example 1 this parameter is significantly higher at low frequencies, while at higher frequencies, the behavior of both Example 1 and commercial PP 2 is similar concerning this parameter.

FIGURE 7 illustrates viscoelastic data for a polypropylene produced according to 20 Example 2 of the invention as compared to commercial PP 2.

FIGURE 8 shows viscoelastic data for the polypropylene of Example 3 as compared to 25 a commercial PP. Higher values for Storage and Loss Modulus of the inventive product indicate a better thermoformability. However, contrary to the product of Example 1, the figures for complex viscosity are high as compared to the commercial PP, indicating inferior extrusion ability.

FIGURE 9 shows viscoelastic data for the polypropylene of Example 4 as compared to a commercial PP. As indicated in Figure 9, the product of this Example does not show the superior properties of the inventive polypropylenes.

30 DETAILED DESCRIPTION

The process for preparing the high melt strength polypropylene according to the invention comprises the steps of:

a) providing at least two polymerization vessels connected in series;

- b) feeding the Ziegler-Natta catalyst into the first vessel of said at least two polymerization vessels;
- c) feeding propylene into each polymerization vessel in such a manner that the pressure under which the propylene is fed decreases from the first to the further vessels;
- 5 d) introducing a molecular weight modifier into at least one of said at least two vessels in a sufficient amount to provide a broad or bimodal molecular weight distribution in the resulting product;
- e) successively transferring the catalyst and the resulting polymerization reaction mixture from the first to each further polymerization vessel, while the products polymerized in each
- 10 polymerization stage are added to and formed on the same catalyst solids, which thereafter will be discharged from the last polymerization vessel;
- f) recovering the polymerization product from the last polymerization vessel.

The most adequate polymerization method for producing the polypropylene of the invention is slurry polymerization in which hydrocarbons such as propane, hexane, heptane and octane are used as diluents. However, other polymerization methods such as reaction in liquid or gaseous propylene are acceptable. Generally the continuous polymerization is carried out at temperatures in the range of 60 to 80 °C and pressures ranging from the atmospheric pressure to 40 Kg/cm² G;

20 The polymerization vessels suitable for carrying out the process of the invention are those normally used in the petrochemical industry, connected in series and in an arrangement so that it is possible to transfer the slurred reaction mixture from one vessel to the following one, a portion of the slurry (liquid phase) being continuously withdrawn and continuously transferred to the next polymerization vessel.

25 The catalyst employed in the present invention is of the Ziegler-Natta type, and although several other types of this class of catalyst find use in the present invention, the preferred catalyst comprises a titanium compound combined to an organoaluminum compound and which has the general formula AlR_mX_{3-m} wherein R is alkyl or aryl, X is a halogen atom and 3<m<1.5. The preferred titanium compound is a titanium composition obtained by the reduction of TiCl₄ with ethyl aluminum halide and heating the reduced product to obtain TiCl₃ in the suitable correct crystalline form. Examples of these compounds are mono- and dialkyl aluminum halides.

30 The total quantity of catalyst employed in the process of the present invention will depend upon the specific desired quantity of the final product and can be promptly determined

by those skilled in the art. The catalyst should be fed to the first polymerization vessel of the series of the at least two polymerization vessels and, thereafter, the catalyst solids are continuously transferred to each further polymerization vessels together with the remaining reaction mixture, while being withdrawn from the last polymerization vessel whereby the solid 5 catalyst particles are coated with the polymers formed thereon in each respective polymerization vessels.

In order to obtain the desired results, the propylene monomer is normally introduced at different pressures in each of the reaction vessels. Usually it is introduced under a pressure of at least 6.0 kg/cm² G in the first polymerization vessel, which thereafter successively decreases 10 of at least 0.1 kg/cm² G in each of the following polymerization vessels. Although the homopolymer of polypropylene prepared according to the process of the invention shows excellent properties, other olefins such as ethylene may also be added to the polymerization step.

Also according to a preferred embodiment of the invention, hydrogen is used as the 15 molecular weight regulator and is fed into at least one of the polymerization vessels, the molar ratio thereof being adjusted so that at the end of the polymerization process, two polymerization portions of different molecular weights are produced, that is to say, a broad or bimodal distribution of molecular weights is obtained so as to produce a final product of suitable rheological properties. The best mode to effect such broad or bimodal molecular 20 weight distribution is by injecting hydrogen into at least one of the polymerization vessels at a molar ratio of the hydrogen flow rate to the propylene flow rate in the range of zero to 0.0002 in the first of the series of polymerization vessels and between 0.0015 and 0.0035 in the following vessels.

The polypropylene obtained according to the above described method presents a higher 25 molecular weight portion and a lower molecular weight portion, the former showing a MI < 1.0 g/10 min as measured at 190 °C/ 10 Kg. The total polymer has a MI < 3.0 g/10 min as measured at 230 °C/ 2.16 Kg. The polymerization is normally adjusted to produce 10 to 35% by weight of the higher molecular weight portion and 65 to 90% by weight of the lower molecular weight portion and preferably the higher molecular weight portion constitutes 15 to 30% by weight of the total polymer. But the best results are achieved when the proportions of the polymerized produced fractions are controlled in each vessel and generally, the quantity of the polymer obtained from the first of the series of said at least two polymerization vessels is adjusted to render a concentration of 10 to 35% by weight of the total polymer produced in the

process.

The amount of diluent, monomer and hydrogen are fed to the polymerization vessels in such a way as the molecular weights of the polymers formed in the respective vessels are successively reduced from the second polymerization vessel on, so as at the end of the process 5 the product shows sufficient difference in molecular weight.

Molded articles prepared with the polypropylene of the invention show an improved uniform distribution of the resin, perfect grooves and excellent shape, and can withstand high operation temperatures with no or small deformation. The polypropylenes may be used alone or, if desired, they can be compounded with conventional fillers such as calcium carbonate, 10 talc, glass fiber, etc, as well as other additives as antioxidants or antistatic agents which are normally employed in a range of 0.1 to 0.5 wt%.

The present invention will now be illustrated by the following examples, which should not be construed as limiting.

15 EXAMPLE 1

The Catalyst was prepared in batches from 230 liters of $TiCl_4$, 550 liters of aliphatic hydrocarbon diluent (2,2,4,6,6 - penta-methyl-heptane) and 2800 liters of an equimolar solution of aluminum diethyl chloride and monoethyl aluminum dichloride diluted to 25 volume 20 % in aliphatic hydrocarbon diluent (2,2,4,6,6 - penta-methyl-heptane). This constitutes solid I to which was added aliphatic hydrocarbon diluent 2,2,4,6,6 - penta-methyl-heptane up to 300 ppm of metallic titanium, as well as diethyl aluminum chloride in order to obtain a molar ratio Al/Ti of nearly 2 so as to prepare the catalyst slurry or diluent phase of which 1800 liters per hour are injected into the first reactor of the series.

25

Polymerization Process

The polymerization slurry was continuously fed to a polymerization vessel R1. Propylene was fed to the polymerization vessels at temperatures of 62, 62, 65 and 75 °C respectively while the pressure was kept at 7.9, 7.5, 7.2 and 5.9 kg/cm²G, corresponding to propylene flow rates 30 of 4,200; 4,100; 2,400 and 20 kg/hour respectively for polymerization vessels R1, R2, R3 and R5 according to appended Figure 1. The hydrogen molar ratio of hydrogen dissolved in propylene fed to R1 was lower than 0.012% while in the other polymerization vessels it was between 0.15 and 0.22%. The polymerization was run during 26 hours. As soon as the

polymer product was discharged from the last polymerization vessel of the series, it was treated with an aqueous isopropyl alcohol solution in order to eliminate catalyst residues. Propylene homopolymer was obtained at a rate of 10,000 kg per hour. Polymer physical properties are listed in Table 1.

5

EXAMPLE 2

In this Example catalyst, temperature and pressure were as in the previous Example. However, propylene flow rates into the various polymerization vessels R1, R2, R3 and R5 10 were respectively 4,200; 4,100; 2,400 and 20,0 kg/hour; the hydrogen molar concentration dissolved in propylene to be added to R1 was 0.02 mole% while in polymerization vessels R2 to R5 it was 0.2 mole%. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield of propylene homopolymer was 10,000 kg per hour.

15

EXAMPLE 3

In this Example catalyst, temperature and pressure were the same as those employed in the polymerization of Example 1. However, propylene flowrates in the various polymerization 20 vessels from R1 to R5 were respectively 5,000, 3300, 2,400, 20 and 20 kg/hour; the hydrogen molar concentration dissolved in the propylene added to R1 was 0.0044 mole % while in the polymerization vessels R 2 to R5 it was 0.3 mole %. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield of propylene homopolymer was 10,000 kg per hour.

25

EXAMPLE 4

In this Example catalyst, temperature and pressure were the same as those employed in the polymerization of Example 1. However, propylene flowrates in the various polymerization 30 vessels from R1 to R5 were respectively 2,200, 5100, 3,400, 20 and 20 kg/hour; the hydrogen molar concentration dissolved in the propylene added to R1 was 0.02 mole % while in the polymerization vessels R2 to R 5 it was 0.2 mole %. The reaction was run during 12 hours; after completion of the reaction and treatment of the polymer with isopropyl alcohol the yield

of propylene homopolymer was 10,000 kg per hour.

The physical properties of the products obtained are listed in Table 1.

TABLE 1

5

		Ex. 1	Ex. 2	Ex. 3	Ex. 4
	Melt Flow Index g/10 min				
	ASTM D-1238; 230 °C/2.16 kg/cm ²	1.56	1.62	1.49	2.36
10	Melt T, °C (DSC) 7	159	159	159	159
	Crystallization T, °C	112	112	112	112
	Molecular Weight Distribution				
15	R.V.(230 °C/5.0 kg); (230 °C/2.16 kg)	5.90	5.50	5.80	5.20
	Stress Strength MN/m ²	33.3	34.7	34.3	33.2
	ASTM D-638				
20	Elongation	92	127	66	77
	ASTM D-638				
	Flexure modulus GM/m ²	1.79	1.71	1.82	1.68
	ASTM D-790				
	Izod Impact Strength	27.5	27.4	28.0	27.0
25	ASTM D-256 23 °C				
	Heat Deflection Temp. °C, 0.45 MN/m ²	91.0	88.0	89.0	88.0
	ASTM D-648 2.82 MN/m ²	3.0	54.0	50.0	50.0
	Vicat Temp. °C, ASTM D-1525	155.0	155.0	155.0	156.0
	n decaline, 135 °C	2.8	2.8	2.4	2.9
30					
	n high molecular weight, decaline, 135°C	6.8	5.5	7.0	5.6
	Melt Flow Index of the high MW fraction, 190 °C, 10 Kg				
		0.4	0.9	0.3	1.1

EXAMPLE 5

In this Example, both a commercial polypropylene and the inventive polypropylene were molded in a Brown HD type engine normally used for the thermoforming of polystyrene.

5 This engine is provided with two furnaces, a superior one and an inferior one. In the superior furnace temperatures were 180, 170 and 170°C. In the inferior furnace temperature was 170°C. The molded sheet had 0.8 mm width, the engine productivity being 8.5 cycles/minute. It could be seen that the inventive polypropylene yielded molded articles of smooth surface and perfect grooves using cycles a bit longer than those of polystyrene (12 vs 8.5 cycles/min) while

10 for a commercial polypropylene, either it was not moldable at all in such a machine, or the molded article did not have good appearance and shape. Thus, the viscoelastic behavior exhibited by the polypropylene of the invention at low frequencies leads to the conclusion that the polypropylene of the present invention shows superior thermoforming qualities. Moreover, the polypropylene of the present invention shows equally better extrusion ability in view of it

15 having lower viscosity at high shear rates (high frequencies). The excellence of the inventive product derives from the combination of excellent thermoforming ability and excellent extrusion ability.

EXAMPLE 6

20

In the same thermoforming machine and under the same conditions as in Example 5, a composition was molded which contained the inventive polypropylene plus 20 wt% of calcium carbonate. The so molded articles had excellent appearance and heat resistance, without deformation. In this case, the productivity of the thermoforming machine is comparable to that obtained in the processing of polystyrene, that is, 11 cycles/min for the filled polypropylene and 12 cycles/minute in the case of polystyrene. This Example demonstrates the excellence of the polymer product of the invention, that is, a propylene polymer processed in machines and cycles normally used for polystyrene.

30 EXAMPLE 7

This Example refers to the "spiral flow test": polypropylene samples (commercial and inventive) of various Melt Indices are melted and passed under pressure within a loop-shaped

mold. In the molded article, for a certain polymer mass is measured the ratio distance/thickness. The results are:

	Sample	Type	Melt Index	Distance/Thickness Ratio
5	1	Commercial PP	1.6	215
	2	Commercial PP	2.2	225
	3	Commercial PP	0.7	190
	4	Example 1	1.6	231
	5	Example 2	1.6	231

10

It can be seen that for commercial PP, the ratio is directly proportional to the M.I., while for Examples 1 and 2, for a similar M.I., the ratio is quite higher, this representing better conditions for the extrusion step of the thermoforming.

15 EXAMPLE 8

Example 8 is illustrated in Figure 2, where it can be seen that for a higher shear rate the inventive polypropylene is less viscous as compared to the commercial polypropylene, this facilitating the extrusion step of the thermoforming.

20

EXAMPLE 9

This Example illustrates the evaluation of the transparency degree for a commercial PP and the inventive polypropylene. Evaluation was effected for pure polymers as well as for polymers compounded with a nucleating agent. It could be seen that the inventive PP is neatly more transparent than the commercial PP, not only per se but also, when compounded with a nucleating agent, the increase in transparency is relatively higher for the inventive PP than for the commercial product.

CLAIMS

1 A high melt strength polypropylene comprising a portion of higher molecular weight and a portion of lower molecular weight, the total polymer having a melt index M.I. < 3.0 g/10 minutes as measured at 230 °C/2.16 kg, and in which the higher molecular weight portion has a melt index M.I. < 1.0 g/10 minutes as measured at 190 °C/10 kg, the polymer comprising from 10 to 35 wt% of the higher molecular weight portion and from 65 to 90 wt% of the portion of lower molecular weight.

2 A polypropylene according to claim 1, wherein the portion of higher molecular weight constitutes from 15 to 30 wt% of the total polymer and the portion of lower molecular weight constitutes from 70 to 85 wt% of the total polymer.

3. A polypropylene according to claim 1, wherein the polypropylene is compounded with from 5 to 40 wt% of mineral fillers such as calcium carbonate, talc, glass fiber and 0.1 to 0.5 wt% of an antioxidant and 0.1 to 0.5 wt% of an antistatic.

4 A process for producing a high melt strength polypropylene comprising the continuous polymerization of propylene in the presence of a Ziegler-Natta type catalyst system and a molecular weight regulator, the molecular weight regulator being used in an amount sufficient so as to produce a polypropylene comprising 10 to 35 wt% of a portion of higher molecular weight and 65 to 90 wt% of a portion of lower molecular weight, the total polymer having a melt index M.I. < 3.0 g/10 minutes as measured at 230 °C/2.16 kg, and in which the higher molecular weight portion has a melt index M.I. < 1.0 g/10 minutes as measured at 190 °C/10 kg.

5. Process according to claim 4, comprising the steps of:

- a) providing at least two polymerization vessels connected in series;
- b) feeding the Ziegler-Natta catalyst into the first vessel of said at least two polymerization vessels;
- c) feeding propylene into each polymerization vessel in such a manner that the pressure under which the propylene is fed decreases from the first to the further vessels;
- d) introducing the molecular weight modifier into at least one of said at least two vessels in a sufficient amount to provide the bimodal molecular weight distribution in the resulting product;
- e) successively transferring the catalyst and the resulting polymerization reaction mixture from the first to each further polymerization vessels, while the products polymerized in each polymerization stage are added to and formed on the same catalyst solids, which thereafter

will be discharged from the last polymerization vessel;

f) recovering the polymerization product from the last polymerization vessel.

5 6. Process according to claim 4, wherein the continuous polymerization is carried out at a temperature between 60 and 80 °C and a pressure ranging from the atmospheric pressure to $40 \text{ kg/cm}^2 \text{ G}$.

7. Process according to claim 5, wherein the pressure of the added propylene is at least $6.0 \text{ kg/cm}^2 \text{ G}$ in the first of said at least two polymerization vessels and decreases of at least $0.1 \text{ kg/cm}^2 \text{ G}$ in the sequence of polymerization vessels.

10 8. Process according to claim 5, wherein hydrogen is used as the molecular weight modifier, the molar ratio of the hydrogen flow rate to the propylene flow rate being in the range from zero to 0.0002 in the first vessel and from 0.0015 to 0.0035 in the following vessels.

15 9. Process according to claim 5, wherein the amount of polymer obtained from the first of the at least two polymerization vessels connected in series comprises from 10 to 35 wt% of the total amount of polymer obtained in the process.

10. Process according to claim 9, wherein the amount of polymer formed in the first of the at least two polymerization vessels in series constitutes from 15 to 30 wt% of the total amount of polymer produced.

20 11. Process according to claim 4, wherein the Ziegler-Natta catalyst comprises an organoaluminum compound combined with a titanium compound in order to form a compound of formula $\text{AlR}_m \text{X}_{3-m}$ wherein R is alkyl or aryl, X is a halogen and $3.0 < m < 1.5$. in the process.

25 12. Process according to claim 11, wherein the catalyst is prepared through reduction of TiCl_4 , which is contacted with aluminum diethyl chloride, ethyl aluminum dichloride and aliphatic hydrocarbon diluent.

13. Process according to claim 12, wherein the aliphatic hydrocarbon diluent is 2,2,4,6,6 - penta-methyl-heptane.

30 14. A process according to claim 4, wherein the portion of higher molecular weight constitutes from 15 to 30 wt% of the total polymer and the portion of lower molecular weight constitutes from 70 to 85 wt% of the total polymer.

15. A molded article produced from the polypropylene of any one of claims 1 to 3.

16. A molded article according to claim 15, produced by thermoformation effected in machines designed for the thermoforming of polystyrene.

FIGURE 1

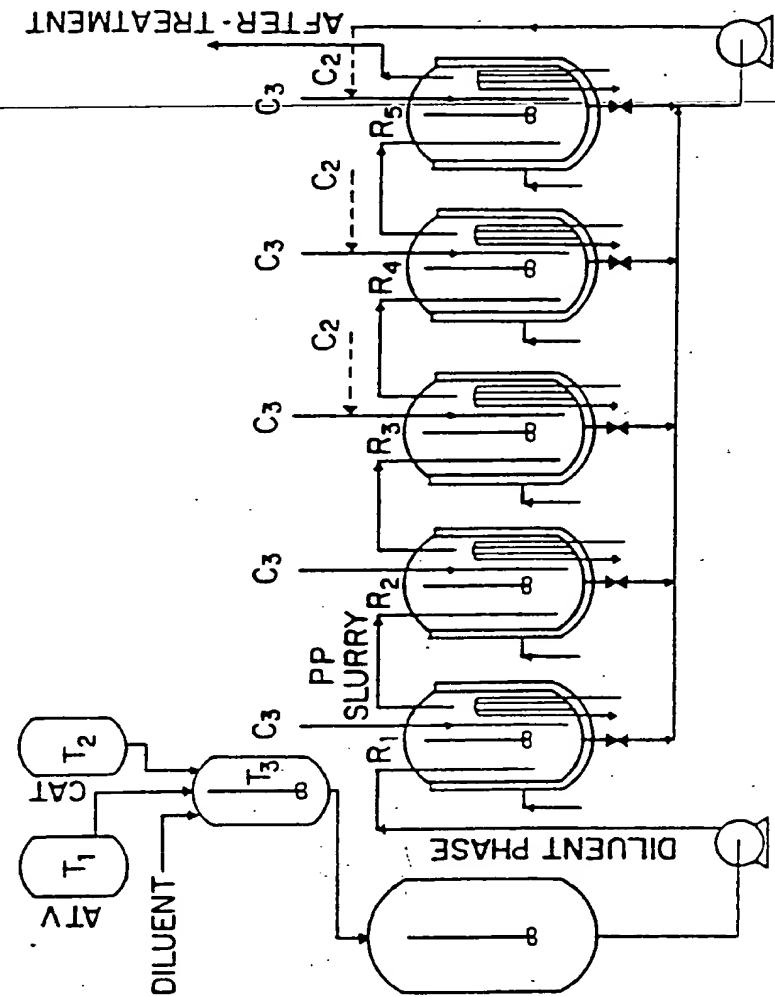


FIGURE 2
VISCOSITY VS. SHEAR RATE $T = 230^\circ\text{C}$

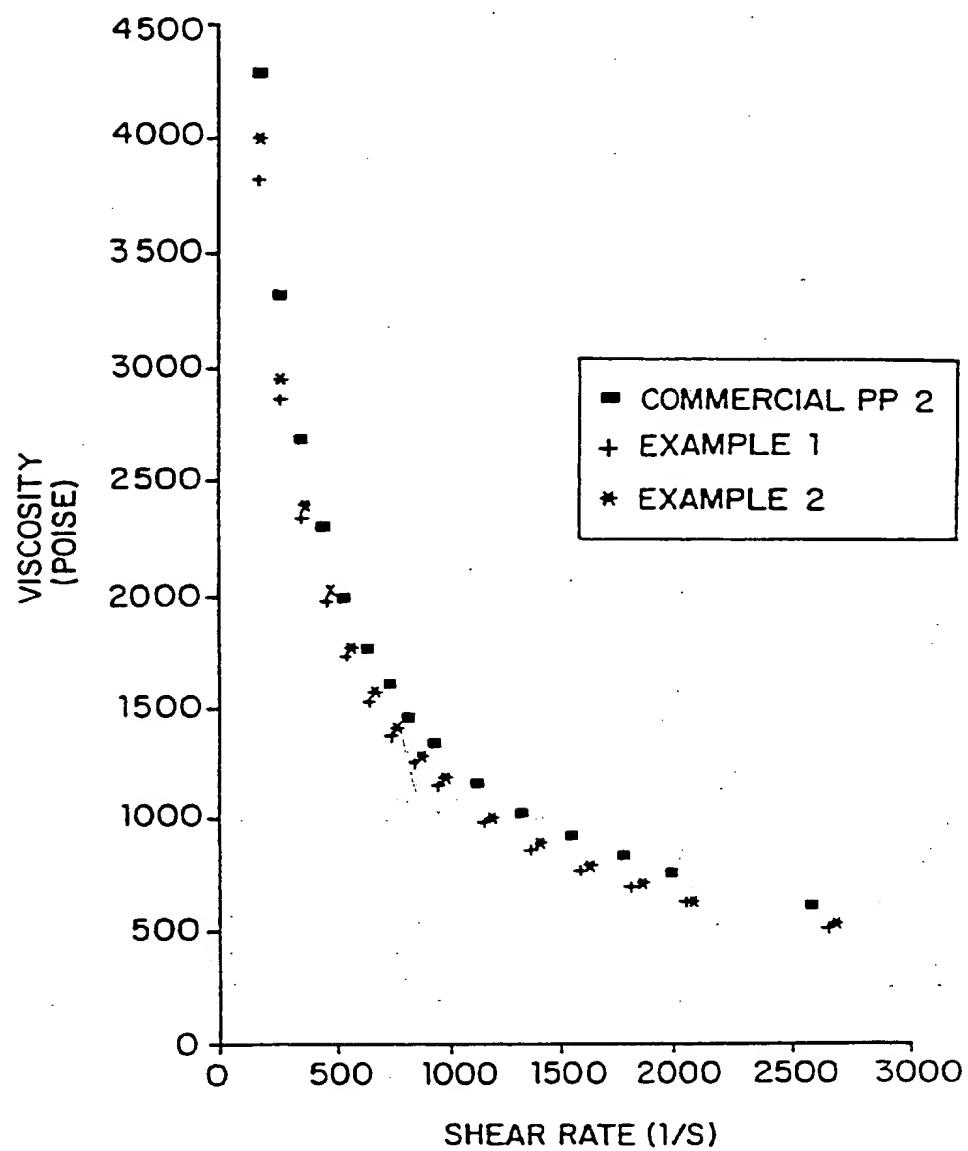


FIGURE 3

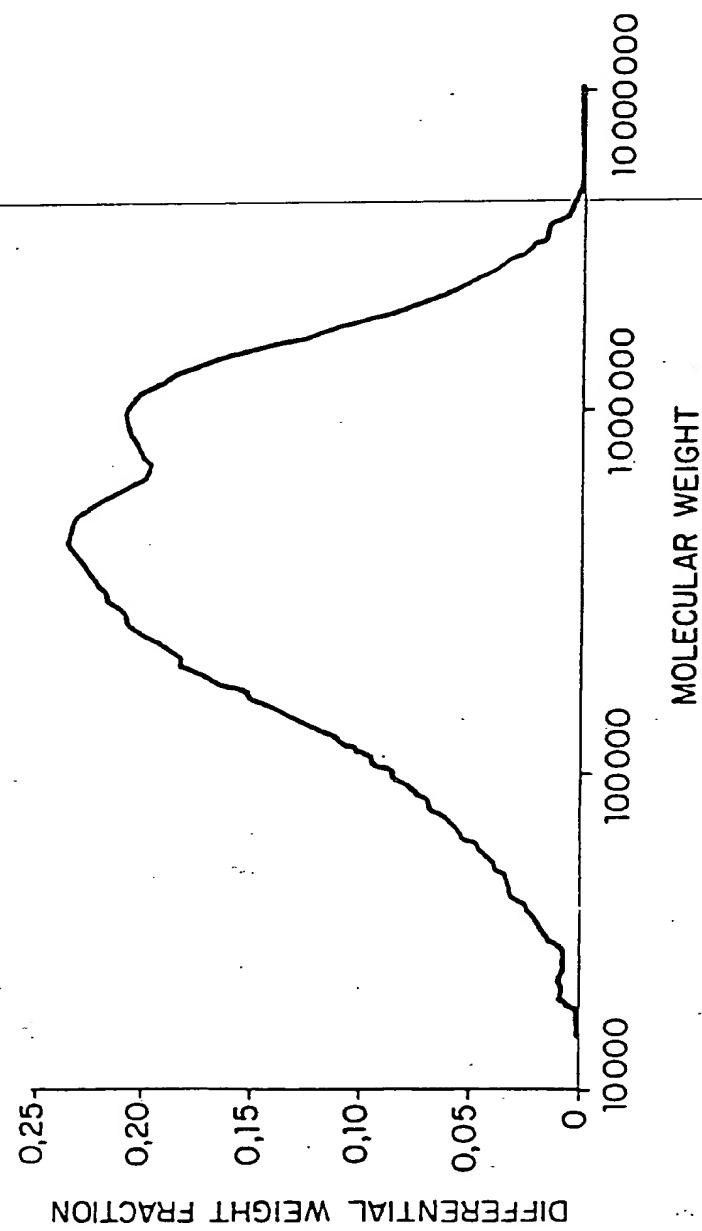


FIGURE 4

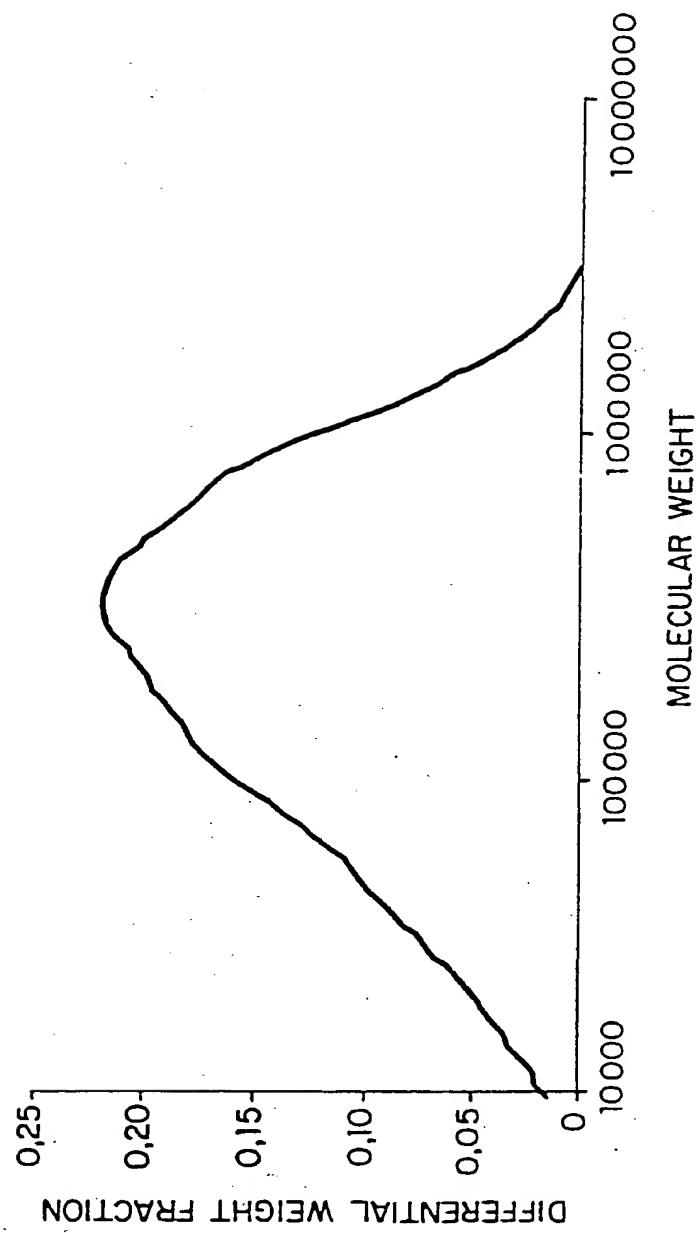
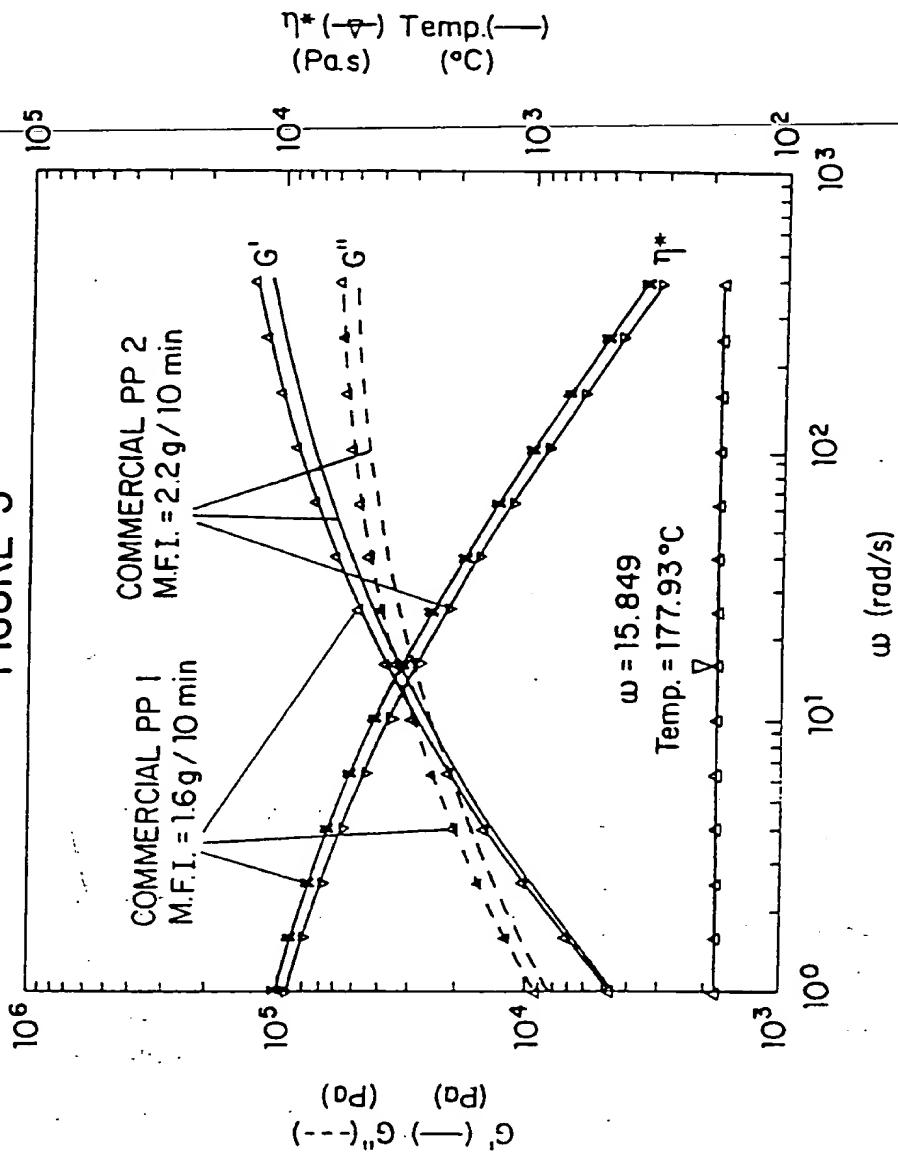
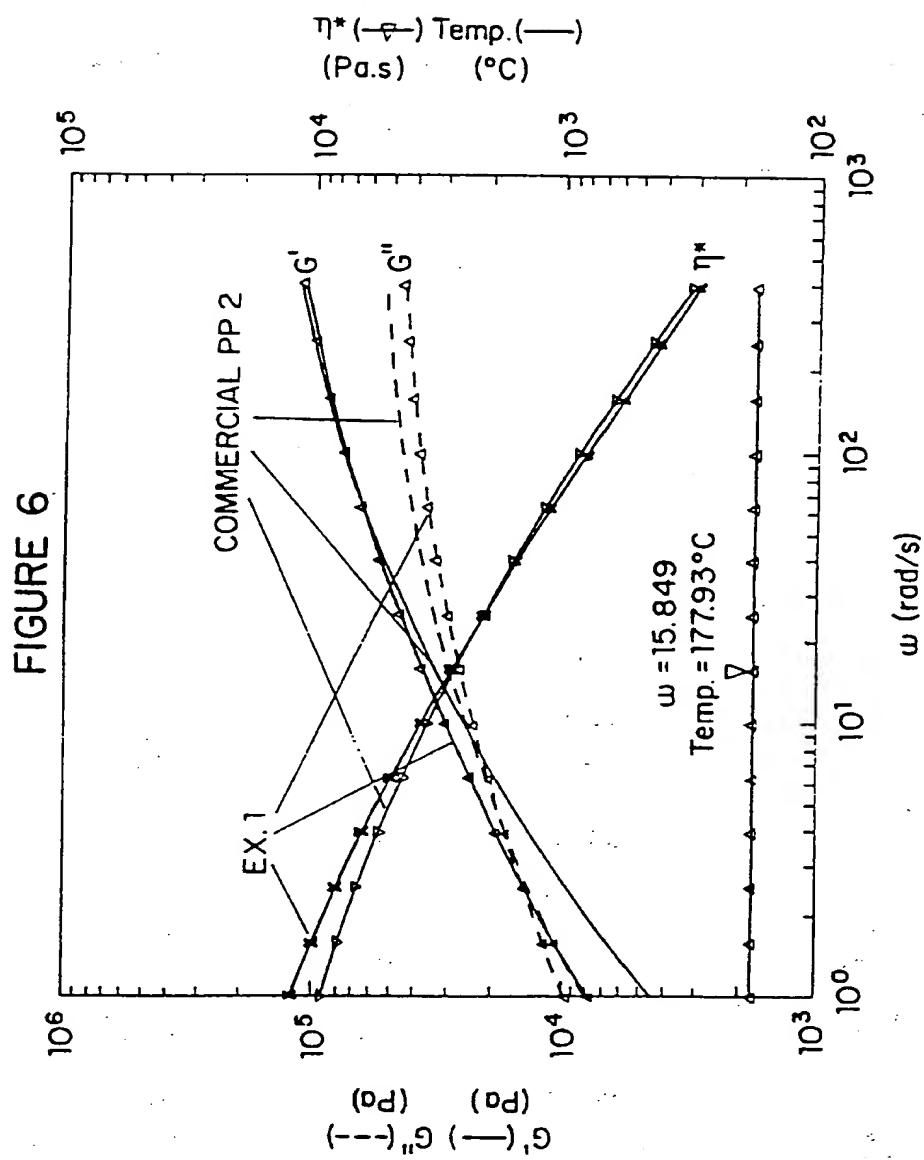


FIGURE 5





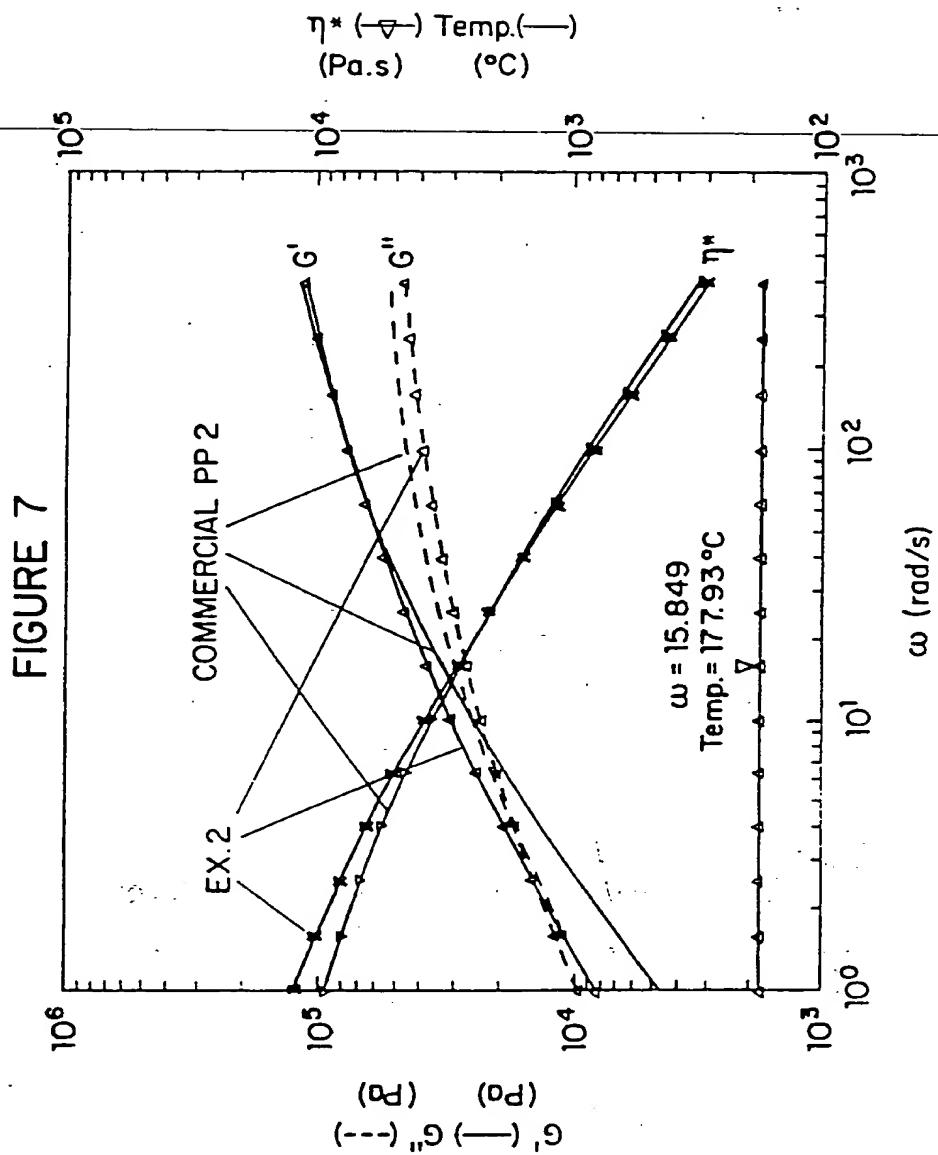
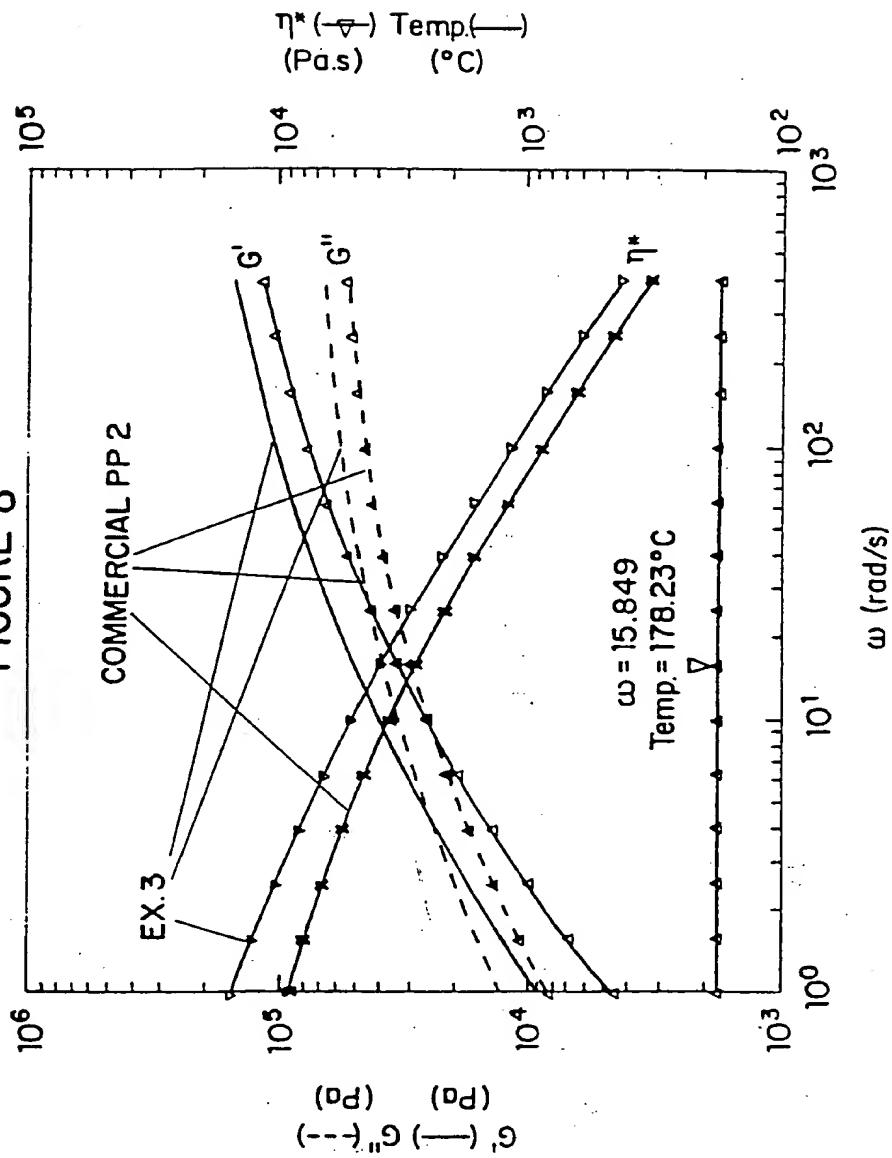
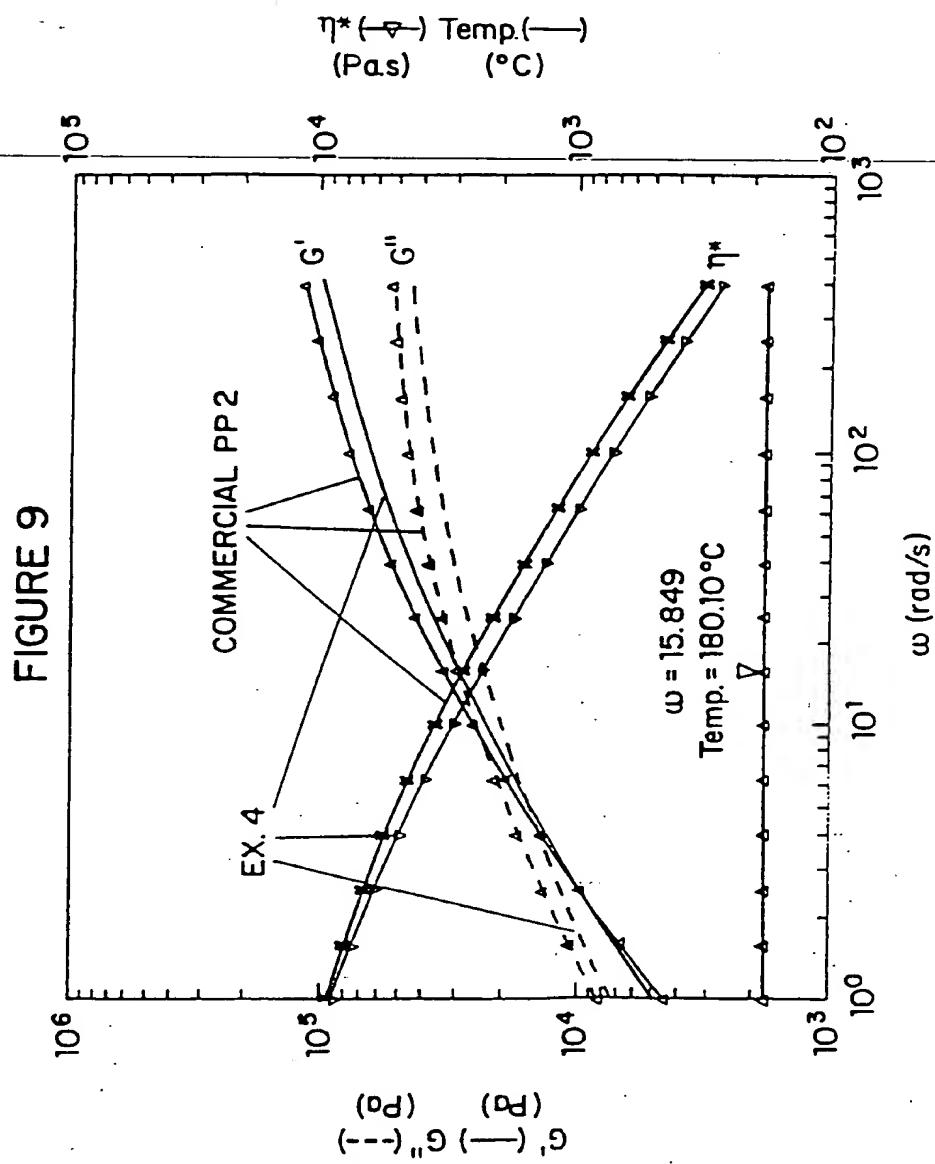


FIGURE 8





INTERNATIONAL SEARCH REPORT

International Application No
PCT/BR 94/00019

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 5 C08F10/06 C08F2/00 C08F4/64		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 5 C08F C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 14718 (HOECHST AKTIENGESELLSCHAFT). 3 October 1991 see claim 1 ---	1-16
X	EP,A,0 098 077 (CHISSO CORPORATION) 11 January 1984 cited in the application see Comparative Example 5 ---	1-3
X	EP,A,0 359 517 (AMOCO CORPORATION) 21 March 1990 see claims 1,2,7 -----	1-3
<input type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
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23 August 1994		05.09.94
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European Patent Office, P.B. 5818 Patentzaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Serravalle, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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